BASIC RESEARCH ON TECHNOLOGY DEVELOPMENT FOR SINTERED CERAMICS

SEMI-ANNUAL TECHNICAL REPORT

March 1976

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20. ABSTRACT *(Continue on reverse side if necessary and identify by block number)*

Fired compacts of "pure" Si_3N_4 powders, having average particle sizes be-
tween 0.15 and 0.4 μ, undergo large ($\simeq$15%) weight losses and considerable
grain growth in the absence of macroscopic shrinkage. The nearly similar
weight loss of Si_3N_4 compacts made from the same starting powder but which
contained different oxygen contents, 3.14 and 0.7 wt%, suggests that the major
portion of material loss is caused by thermal decomposition of Si_3N_4 and not by
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an oxygen-removal reaction. This information leads to the conclusion that the sintering of "pure" Si_3N_4 is prevented by high vapor transport and/or thermal decomposition.

The use of high nitrogen pressures ~5 MPa (50 atm) and low oxygen partial pressures ~100 pPa (10^{-15} atm) at temperatures above 1800°C does not permit more than 1% linear shrinkage in "pure" Si_3N_4 compacts but considerably reduces the weight loss (thermal decomposition below that found when 0.1 MPa (1 atm) of nitrogen is used. Since grain growth and pore growth occur without much shrinkage, it is concluded that vapor phase transport and/or thermal decomposition still dominate structural transformation during firing.

A puzzling result in sintering is the formation of weak intergranular bonds in compacts of pure Si_3N_4 fired at high temperature in nitrogen pressures between 0.1 and 50 MPa. In addition, the conventional hot pressing of the same Si_3N_4 powders gives rise to crumbly specimens. The poor intergranular bonding may be related to thermal decomposition effects or to impurities such as chlorine. It will be necessary to determine the precise origin of this weak bonding.

Results of the hot pressing of various Si_3N_4 powders (particle size ≥ 0.1 µ) at high pressures (5 GPa) show that a temperature of about 1550°C is necessary for the attainment of densification. If it is assumed that this densification occurred by a diffusion process, then it is expected that temperatures higher than 1550°C will be required to sinter pure Si_3N_4. Some of the high pressure experiments which yielded dense compacts with high Knoop hardness are encouraging. These results indicate that specific pressing conditions can yield intergranular bonding and the identification of all the factors leading to such bonding may allow densification at lower and practical pressures.

The addition of small amounts (≤ 5 wt%) of boron and both boron and carbon to Si_3N_4 permits the development of a high surface area (10-33 m^2/g), fine-grained microstructure but produces essentially no macroscopic shrinkage at 1800°C in nitrogen. For the compositions studied thus far, there is still insufficient diffusion of Si and N in Si_3N_4 to allow densification by solid state sintering.

The need for Si_3N_4 powder with higher specific surface area and purity than that commercially available led to the synthesis, on a laboratory scale, of amorphous Si_3N_4 powders with specific surface areas as high as 80 m^2/g by the reaction between silane and ammonia. At temperatures above 600°C, it is difficult to prepare Si_3N_4 powders free of silicon. Powders containing free silicon cannot be completely nitrided at temperatures below 1400°C in nitrogen. However, preliminary results indicate that Si_3N_4 powder free of elemental silicon and low in oxygen can be synthesized by the reaction between silane and ammonia in a temperature interval between about 530° and 570°C.

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SUMMARY

Work reported on the previous contract period in this program was specifically directed towards a detailed analysis of the sintering behavior of two typically covalently bonded materials, β-SiC and Si metal. Silicon metal represented an intermediate material, previously unsinterable, to which the understanding recently developed for the dense sintering of β-SiC could be applied. It was, in fact, demonstrated that the application of this understanding resulted in procedures by which silicon metal could be pressureless sintered to the dense form. This accomplishment provides the way for direct attack on the major objective of the program -- the densification of silicon nitride in the pure phase form or at least in a form whereby second phases would not limit high temperature properties. Two approaches towards this objective are available. The first approach entails the direct densification and shrinkage of preforms of Si_3N_4 powder. The second entails the densification and shrinkage of a preform of silicon metal and its subsequent conversion to Si_3N_4 by nitridation.

Work during the present contract period has mainly followed the first approach and has been directed towards the evaluation of commercial Si_3N_4 powders and means to chemically adjust them, the direct synthesis of pure Si_3N_4 powders and their evaluation, determination of the sintering response of such powders under hot pressing diamond forming conditions and under both low and high nitrogen pressures without applied mechanical pressures. In addition, experiments have been made to determine the effects of an initial set of chemical additives on pressureless sintering behavior.

In general, relative to the sintering (densification) of Si_3N_4 powders without the aid of mechanical pressure, the investigations provide little evidence of intergranular bonding accompanied by shrinkage. Densifications in excess of 1% were not observed even at temperatures in excess of 1800°C and nitrogen pressures of 50 atm. At diamond forming pressures, which yielded full density compacts, some evidence of intergranular bonding in selected samples was observed. In these cases, the bonding may have been a consequence of unintentional additives which require further investigation and may provide a route to the overall densification problem. Complementary with this experimentation, procedures have been developed which show improved efficiencies in

limiting Si_3N_4 volatilization losses at high temperatures and a promising method for the preparation of low oxygen, silicon free powder has been developed. It is concluded that the atomic mobilities are so low in Si_3N_4 that temperatures well in excess of 1800°C will be necessary for its densification without pressure. This result reinforces the expectation of remarkable high temperature mechanical properties of this material in pure form.

Present work is outlined and directed towards conventional hot pressing of the developed powder utilizing solute or high temperature precipitate additives and to detailed investigations of the second approach listed above -- silicon presintering followed by nitridation.

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I. RESEARCH OBJECTIVES

The objectives of this research program are to identify the factors which govern the sintering of covalent ceramics, especially Si_3N_4, and to apply this knowledge towards developing procedures for sintering dense Si_3N_4 into components suitable for use in high temperature engines. In order to meet these objectives, experiments will be conducted to elucidate what physical and chemical processes prevent and/or aid the densification of Si_3N_4 and to determine by what means these processes may be appropriately modified, if necessar

The main thrust of this research is aimed at attempting to densif   ure or doped Si_3N_4 by a solid state sintering process. The ability to prepai   ise Si_3N_4 with strength levels adequate for turbine parts by sintering wo   greatly enhance the prospects for enabling fabrication of truly high performai _   amics for high temperature engine applications.

II. GENERAL BACKGROUND

Silicon nitride is a material which exhibits unique chemical and mechanical properties. In a previous report under this program (ONR Contract N00014-74-C-0331) the resistance to creep and oxidation of this material in pure phase form was determined and shown to be outstanding. These characteristics, coupled with low thermal expansivity and relatively low elastic modulus, substantiate the selection of this material as an optimum candidate for many high temperature structural applications.

Silicon nitride is, however, a material which exhibits a high degree of covalent bonding, and similar to many other such materials, presents many severe obstacles to its preparation by mechano-chemical processes, familiar to the ceramist, into dense, sound structures.

Experience indicates that there exists four main obstacles, specific to Si_3N_4, which hinder the application of solid state sintering principles to the densification of Si_3N_4 without property degrading phases and additives. First, the decomposition temperature of Si_3N_4 is only around 1900°C and thus large weight losses by vapor transport and thermal decomposition is anticipated and observed. This characteristic suggests that very fine particle size Si_3N_4 powders must be prepared and utilized to enhance volume and/or rain boundary

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diffusion at somewhat lower temperatures. Additionally, this characteristic virtually demands that high nitrogen pressures, perhaps in the kilobar ranges, may be required to suppress decomposition. Secondly, the judicious search and use or elimination of solute additives is indicated to achieve matter transport mobility sufficient to promote grain boundary formation yet insufficient to significantly degrade high temperature properties. Finally, the $\alpha \to$ Si$_3$N$_4$ transformation, which leads to elongated grain morphologies and bridging particle structures, is considered to be undesirable and means should be sought for its inhibition or control.

From the above it is clear that both the physical and chemical characteristics of starting powders is critical to the achievement of solid state densification of Si$_3$N$_4$. The following initially addresses this subject and continues with various approaches for their densification.

III. Si_3N_4 POWDERS

A. Characterization

Most of the experimental work presented in this report was accomplished with the use of two high purity (exclusive of oxygen and chlorine contamination) Si_3N_4 powders purchased from GTE Sylvania. One powder, identified as SN-402, was primarily amorphous and had a purity >99.99% by weight with respect to metallic contamination. The major metallic impurity is molybdenum, 0.01 wt%. An oxygen content of 3.14 wt% was measured by neutron activation analysis, and agrees well with the value of ~3 wt% measured by the supplier. X-ray fluorescence revealed the presence of about 1 wt% Cl, a value in agreement with that given by the supplier. The chlorine contamination apparently arises from the synthesis of Si_3N_4 by the reaction between $SiCl_4$ and NH_3. X-ray diffraction analysis using a Debye-Scherrer camera and 15 hrs of exposure time showed that the SN-402 powder contained a trace amount of α-Si_3N_4, a trace of free silicon and no crystalline or amorphous SiO_2 or ammonium chloride. Also, there were very weak, unidentified diffraction lines at d-spacings of 5.60 Å, 3.29 Å, 2170 Å and 2.63 Å, which may indicate possible traces of some (Mo,Cr) silicides. The lattice parameters of the α-Si_3N_4 were a_o = 7.752 A and c_o = 5.614 Å.

The particle size and shape were determined by specific surface area measurements and by observations by scanning electron microscopy (SEM). The SEM photomicrograph presented in Fig. 1 shows that the powder particles are uniformly equiaxed, having a size of about 0.2 µ, and appear to be at least partially aggregated. The specific surface area, measured by the single point B.E.T. method, was 12.8 m^2/g and corresponds to an average particle size of 0.15 µ. The B.E.T. method is, of course, a more reliable method of measuring the average particle size of submicron powders.

The second Si_3N_4 powder was also purchased from GTE Sylvania and was identified as SN-502. This powder had a purity greater than 99.9% with molybdenum being the major metallic contaminant of about 0.01 wt%. The oxygen and chlorine content of this powder were 1 wt% and <0.04 wt%, respectively. This SN-502 powder was crystalline, as determined by X-ray diffraction analysis, and contained about 94% α-Si_3N_4 and 6% β-Si_3N_4. No forms of SiO_2 or Si_2ON_2 could be detected by X-ray analysis. The lattice parameters of the α-Si_3N_4 were nearly the same as that measured for the α-Si_3N_4 phase in the SN-402 powder.

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Figure 1. Scanning Electron Micrograph of Particles
of the SN-402 Si_3N_4 Powder   5000X

The average particle size, as determined from the specific surface area measurement of 4.5 m^2/g, was 0.42 μ. Particles of α-Si_3N_4 were equiaxed but particles of β-Si_3N_4 were elongated with aspect ratios as high as 20:1 in some cases.

B.   Oxygen Removal From Si_3N_4 Powder

1.   Thermal treatments

The high oxygen content of $\sim$3 wt% in the starting Si_3N_4 powders is believed to be undesirable because its presence can lead to intergranular silicate phases in the fired material which have deleterious effects on high temperature mechanical properties. Wright and Niez[4] reported that as much as 50% of the oxygen could be removed by thermal treatment at 1600°C under a nitrogen pressure of 4 kPa (30 torr) for several types of starting powder. These powders had initial specific surface areas between 2 and 4 m^2/g, and particle growth and aggregation occurred during firing which reduced the sinterability of the starting powder. The powder used in this present study, SN-402, has a specific surface area of 12 m^2/g and is about 4 times finer than those powders investigated by Wright and Niez. The application of a preliminary heat treatment schedule was found to cause a 75% reduction in the specific surface area of the powder which significantly reduces the sinterability of the powder. Therefore, other heat treatment schedules were explored.

The removal of oxygen from Si_3N_4 powders at high temperatures probably occurs by one or both of the following possible chemical reactions based on thermodynamic calculations:

$$SiO_2(s) \rightarrow SiO(g) + 1/2\ O_2(g) \tag{1}$$

$$3SiO_2(s) + Si_3N_4(s) \rightarrow 6SiO(g) + 2N_2(g) \tag{2}$$
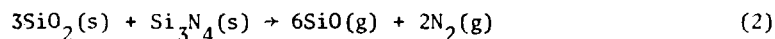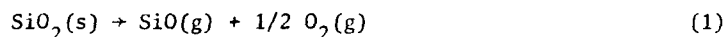
The oxygen is assumed to be present primarily in the form of discrete SiO_2 particles (SiO_2 particles are observed in polished sections of dense samples prepared from SN-402 and SN-502 Si_3N_4 powders formed under diamond forming conditions) or in the form of a passivation layer of SiO_2 surrounding the Si_3N_4 particles. In the latter case reaction can occur at the Si_3N_4/SiO_2 interface with the formation of SiO and N_2 gases. This reaction can proceed only at a reasonable rate if the product gases escape through microcracks at the reaction interface.

By using the free energies of formation available in the JANAF tables[5],

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calculations reveal that for reaction (1) at 1700°K

$$P_{SiO} \cdot P_{O_2}^{\frac{1}{2}} = 6.5 \times 10^{-12}$$

and for reaction (2) at 1700°K

$$P_{SiO}^6 \cdot P_{N_2}^2 = 8 \times 10^{-18}$$

These calculations show that by firing the starting powder in dry H_2 (dew point = -60°C) the partial pressure of oxygen is 5 fPa (5×10^{-20} atm) at 1700°K. Consequently, there is a strong tendency to form an appreciable vapor pressure of SiO gas, $P_{SiO} \approx 3$ kpA (3×10^{-2} atm), by reaction (1). Reaction (2) should also proceed during hydrogen firing or when H_2/N_2 mixtures or vacuum are used. Furthermore, by firing in a vacuum of 1.3 mPa where the P_{O_2} is ~0.3 mPa and the P_{N_2} ~1 mPa, there will be a tendency to form SiO gas by reaction (1).

The results of the effect of hydrogen and vacuum firing on weight loss, specific surface area and residual oxygen content of SN-402 Si_3N_4 powder are presented in Table I and Figs. 2 and 3.

In both firing treatments, 5 grams of Si_3N_4 powder was spread out on a tungsten sheet in an identical manner and then fired in a tungsten furnace. Over the temperature range investigated the weight loss increased and the specific surface area decreased with increasing temperature. The oxygen content was reduced from 3.14 to 0.7 wt% by firing under vacuum (1.3 mPa) for 1 hr at 1400°C, representing a 78% reduction in the oxygen content of the powder. The disadvantages of this heat treatment schedule are that the specific surface area decreases from 13 to 5.8 m²/g and the weight loss was very high, near 30%. This high weight loss can only be accounted for by the thermal decomposition of Si_3N_4 into Si and N_2 (the equilibrium P_{N_2} = 130 Pa (1.3×10^{-3}) atm at 1700°K) because the maximum weight loss expected for the SN-402 powder containing ~3 wt% oxygen is about 5.6 wt% according to reaction (1) and 10 wt% according to reaction (2), assuming all the oxygen is removed and no other weight loss mechanisms exist. By firing for 1 hr in dry H_2 at 1500°C the oxygen content was reduced from 3.14 to 2.48%. A large weight loss of 18% occurred and depended on the thickness of the powder bed used, with smaller weight losses being observed for thicker powder beds. The specific surface area of the Si_3N_4 powder heat treated in hydrogen was always higher than that
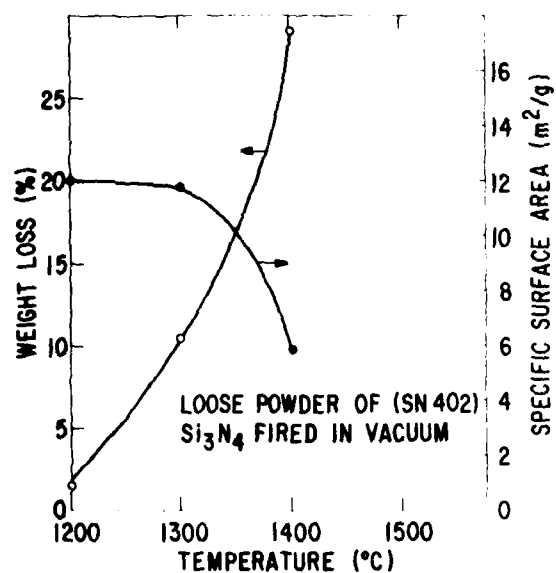
Figure 2. Weight Loss and Specific Surface Areas as a
Function of Temperature for Loose Powder of
SN-402 Si_3N_4 Fired in Vacuum for 1 Hr
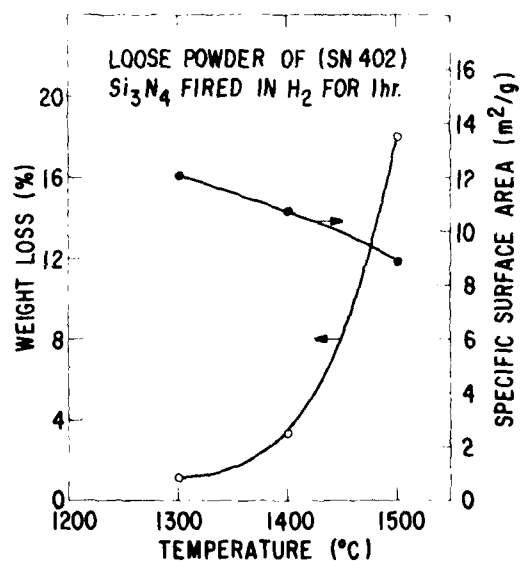
Figure 3. Weight Loss and Specific Surface Area of Loose Powder
of SN-402 Si_3N_4 Fired in Dry Hydrogen for 1 Hr

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treated in vacuum at temperatures above 1300°C and attained a value of 8.8 m^2/g at 1500°C, corresponding to a 32% reduction in the surface area.

The primarily amorphous Si_3N_4 (SN-402) powder remained white when fired in H_2 at 1300 and 1400°C but turned light grey in color when fired at 1500°C. Under vacuum conditions, the powder was essentially white at 1200°C but turned pale yellow at the higher temperatures. X-ray diffraction analysis showed that powder fired at or above 1400°C consisted primarily of α-Si_3N_4 which was more poorly crystallized when hydrogen-treated rather than vacuum-treated. A small percentage ($\sim$5-10%) of poorly crystallized β-Si_3N_4 and a slight trace of free Si were detected in powder vacuum fired at 1400°C.

It was first thought that changes in oxygen content produced by a given thermal treatment might be detected by infrared spectroscopy. After a specified thermal treatment the Si_3N_4 powder was placed in a N_2 glove box, weighed in a proportion of 2 mg of Si_3N_4/g KBr and the mixture pressed into a thin, transparent disc for infrared analysis. Infrared absorption spectra are given in Fig. 4. The spectrum for the "as-received", primarily amorphous Si_3N_4 (SN-402) powder which contains 3.14 wt% oxygen, is illustrated in Fig. 4A. Small absorption bands located at approximately 2.9 and 6.2 microns are due to vibrations of O-H bonds and arise because of the presence of H_2O in the KBr material. A large broad absorption band due to Si-N vibrations is centered at about 10.5 microns and contains some structure between the wavelengths of 11 and 12 microns. Absorption bands also exist at wavelengths beyond about 14 microns, but they are less intense and sharp. There is no evidence of any absorption bands due to Si-O vibrations because, as illustrated in Fig. 4E for (Cabosil)SiO_2, the major Si-O absorption bands occur between about 8 and 10 microns and, if weak, will be masked by the much stronger Si-N absorption band(s) centered at 10.5 microns. The infrared absorption spectrum of powder fired in vacuum at 1400°C and containing only 0.7 wt% oxygen is given in Fig. 4B. All the absorption bands related to the Si_3N_4 structure appear to be sharper and may be attributed to the better crystallinity (α-Si_3N_4) of the vacuum-fired, Si_3N_4 powder as compared to the amorphous starting powder. This interpretation is further reinforced by comparing this spectrum to that for powder fired at 1400°C in hydrogen (Fig. 4C). This hydrogen-fired powder, which is composed of poorly crystallized α-Si_3N_4 and contains nearly 3 wt% oxygen, also shows the

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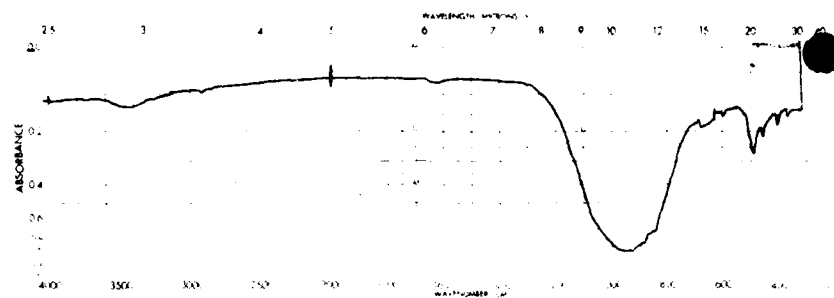
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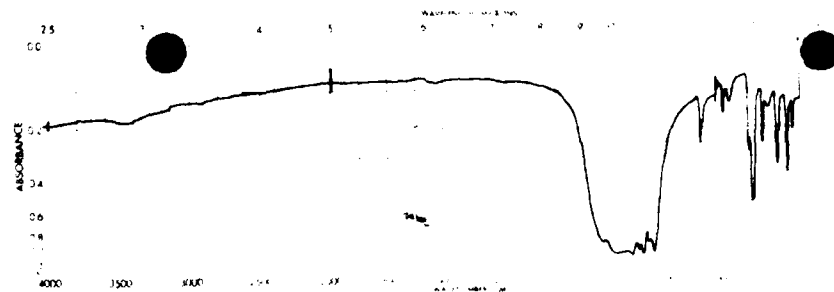
(B)
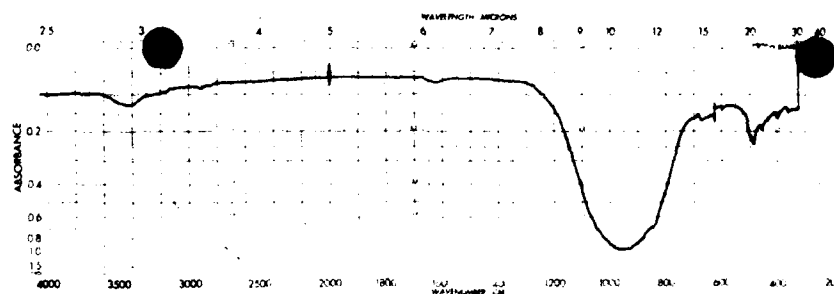
(C)

Figure 4.   Infrared Spectrum for (A) the "As-Received" SN-402
Si₃N₄ Powder, (B) the "As-Received" Si₃N₄ Powder
Vacuum-Fired at 1400°C for 1 Hr, (C) the "As-Received"
Si₃N₄ Powder Hydrogen-Fired at 1400°C for 1 Hr,
(D) the "As-Received" Si₃N₄ Powder Hydrogen-Fired at
1400°C for 1 Hr and Then Removed From the Furnace
and Cooled in Air, and (E) (Cabosil) SiO₂

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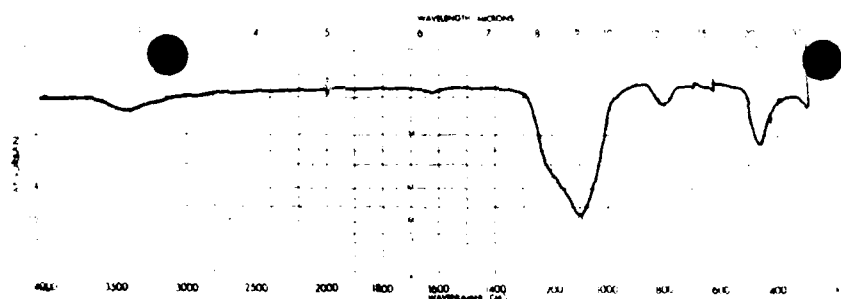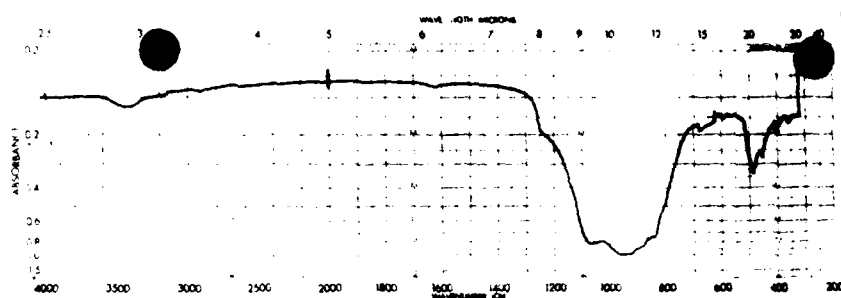
(E)

Figure 4. (Continued)

same large, broad peak as observed for the "amorphous powder illustrated in Fig. 4A. By accident, there was only one case where oxygen was detected in Si_3N_4 powder by infrared spectroscopy. This occurred when Si_3N_4 powder was fired in hydrogen at 1400°C and then removed from the furnace while still hot and cooled in air. An infrared absorption spectrum of this powder presented in Fig. 4D shows two shoulders on the main absorption band between 8 and 10 microns which agree well with the positions of the Si-O absorption bands for SiO_2 shown in Fig. 4E. The oxygen content of this Si_3N_4 was not determined. The above results demonstrate that infrared spectroscopy cannot be conveniently used to measure small changes in oxygen content in Si_3N_4 powders containing less than 5 wt% oxygen.

Another attempt of removing oxygen from SN-402 Si_3N_4 powder was to separately place 1 g of powder and about 0.2 g of Zr metal into one end of an 18 cm long fused silica tube closed on one end, evacuating to 130 Pa, backfilling with 17.3 kPa of argon and then sealing off the other end. This closed tube was placed in a temperature gradient furnace with the sample end at 1400°C and the opposite end at 1050°C. In this way the oxygen partial pressure inside the tube is controlled by the Zr/ZrO_2 reaction and is less than 10^{-21} Pa ($<10^{-26}$ atm). Such a low oxygen partial pressure permitted distillation of SiO vapor from the Si_3N_4 powder, which was at 1400°C, and the subsequent condensation of it at the opposite cooler end of the tube at 1050°C. During the attempt to remove the powder sample from the closed tube, it was virtually impossible to prevent SiO_2 flakes from contaminating the powder. After cutting open the tube in the best possible manner, the resulting powder was analyzed for oxygen and was found to contain 9 wt% oxygen. This method of oxygen removal appears to be impractical because of the difficulties experienced in sample removal after firing.

2. Leaching treatment

A few experiments were carried out to determine if it was feasible to dissolve the SiO_2 phase from the amorphous (SN-402) Si_3N_4 powder. Sixteen milliliters of concentrated HF was slowly added to a water slurry (1.6 g Si_3N_4/ 16 ml) in a teflon beaker until the onset of gas bubble formation. A strong exothermic reaction occurred. After 3 minutes the system was heavily diluted with distilled water and filtered and washed. The percent recovery was only 5%, obviously indicating that the submicron Si_3N_4 particles also dissolve in the

HF solution. In order to suppress the dissolution of Si_3N_4, the leaching time was decreased by diluting the system at the time when the first gas bubbles were visually observed. The percent of the powder recovered by this method was only 25%. The specific surface area of this leached powder was 10.8 m^2/g which is significantly lower than that (13 m^2/g) of the starting powder. By considering the reactivity of amorphous Si_3N_4 with HF and the observation that the oxygen content of the leached powder is 2%, as compared to a value of 3.14 wt% for the unleached powder, it appears that leaching with HF acid will not be a viable method of significantly reducing the oxygen content.

TABLE I

The Effect of Heat Treatment in Vacuum and

Hydrogen on Weight Loss, Specific Surface Area and

Oxygen Content of Si_3N_4 Powder (SN-402)

Heat Treatment	$\Delta W/W_o$(%)	$S(m^2/g)$	Oxygen Content*(%)
None	0	13	3.14
1200°C-1 hr-Vac	1.8	12	N.D.
1300°C-1 hr-Vac	10.5	10.7	2.40
1400°C-1 hr-Vac	29	5.8	0.70
1300°C-1 hr-H_2	1.0	12	3.15
1400°C-1 hr-H_2	3.2	10.8	3.05
1500°C-1 hr-H_2	18	8.8	2.48

N.D. = Not Determined
* Neutron Activation Analysis

3. Summary

The thermal and leaching experiments conducted on the removal of oxygen from a Si_3N_4 powder of high specific surface area (13 m^2/g) strongly indicate that it is extremely difficult to remove a large fraction (>80%) of the oxygen without sacrificing large amounts of material losses and/or considerable reduction in the specific surface area of the powder which is highly undesirable from the sintering viewpoint. Based on the premise that oxygen (SiO_2) in the starting powder is mostly responsible for the formation of undesirable silicate phases which degrade the high temperature, mechanical properties of dense Si_3N_4, it becomes apparent that one of the best methods of controlling or minimizing the oxygen content in fine Si_3N_4 powders is by careful powder preparation. We are currently investigating the preparation of Si_3N_4 powder having high surface area and low oxygen content by the reaction between silane and ammonia at temperatures above 500°C. This method of powder preparation is discussed in detail later.

IV. SINTERING BEHAVIOR OF Si_3N_4 WITHOUT MECHANICAL PRESSURE

A. Normal Pressures

1. Powder forming and firing conditions

Most powder compacts were formed from the "as-received" powders by die-pressing $\frac{1}{2}$ g of powder in a 1.6 cm diameter die at 62 MPa and then isostatically pressing the resulting disc at 200 MPa. The green density of SN-402 compacts was ~37% of the theoretical value (3.18 g/cm^3) and that of the SN-502 compacts was about 40%. Several of the heat treated powders which had lower oxygen contents were also fabricated into discs in the same manner as described above.

Most of the firing experiments were performed in a programable Mo-wound resistance furnace inside of which contained an Al_2O_3 tube, closed on one end, The Si_3N_4 compact was placed on a SiC setter which rested on an Al_2O_3 setter, and the assembly pushed inside the Al_2O_3 tube into the hot zone of the furnace operating at 1000°C in a flowing nitrogen atmosphere (15 cm^3/sec). The thermal cycle treatment consisted of a heating rate of 4°C/min to the desired soak temperature, a soak time of 30 min and a cooling rate of 4°C/min down to 1000°C. A few samples were fired in (N_2-5% H_2) gaseous mixture.

2. Characterization of fired Si_3N_4 compacts

The fired compacts were weighed and then measured for dimensional changes. Parts of the fired compact were (1) lightly crushed with a SiC mortar

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and pestle to make coarse powder for surface area measurements, (2) completely powdered for phase analysis by X-ray diffraction, and (3) fractured for the observation of microstructure by SEM. Occasionally, a whole sample was submitted for an oxygen analysis by the neutron activation method.

3. Results

The specific surface area and weight loss of compacts of SN-402 and SN-502 powders are shown as a function of temperature in Figs. 5 and 6. In Fig. 5 the Si_3N_4 (SN-402) compacts began to exhibit surface area reduction between 1200 and 1300°C and had the greatest surface area reduction between 1400 and 1600°C. The specific surface area after firing at 1400°C for 30 min in nitrogen is about 13.5 m^2/g and at 1600°C for the same time is 1.6 m^2/g. From 1600 to 1800°C the specific surface area changes very slowly from 1.6 m^2/g to 0.8 m^2/g.

It should be pointed out that the apparent specific surface area of lumps of a "green" compact of SN-402 powder was 15.5 m^2/g as compared to 13 m^2/g for the unpressed powder. In addition, compacts fired at 1100 and 1200°C had a specific surface area of 17.2 m^2/g which is higher than that of the green compact. These differences are probably attributed to capillary condensation of nitrogen in the very fine (<50 Å) pores created in the green compact and in compacts fired at 1100 and 1200°C.

The weight loss data presented in Fig. 5 shows there is little ($\leq 1\%$) weight loss up to 1400°C, a rapid increase in the weight loss between 1400 and 1600°C from about 1 to 12.5%, and a slow increase in weight loss from 12.5% at 1600 to 15% at 1800°C. The weight loss of a compact prepared from vacuum-fired SN-402 powder containing 0.7 wt% oxygen was still very high, nearly 13% at 1700°C.

The specific surface area and weight loss data as a function of temperature (Fig. 6) for Si_3N_4 compacts made from SN-502 powder (94% α-Si_3N_4) also showed a major amount of weight loss in the same temperature region where a large reduction in specific surface area occurred. The specific surface area began to decrease at a much higher temperature (~1500°C) than that (~1250°C) observed for the SN-402 powder which had a much higher, initial specific surface area. However, for the SN-502 specimens the beginning of weight loss occurred at the same temperature, 1400°C, as that observed for SN-402 specimens. The average weight loss for the SN-502 compacts fired at 1800°C was about 12% as compared to a value of 15% for the SN-402 compacts.

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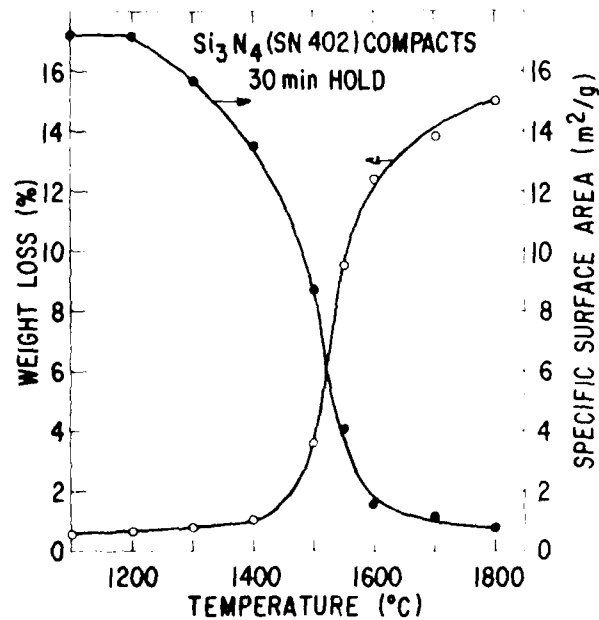
Figure 5. Weight Loss and Specific Surface Area As a Function
of Temperature for (SN-402) Si_3N_4 Compacts Fired
for 30 Min in N_2
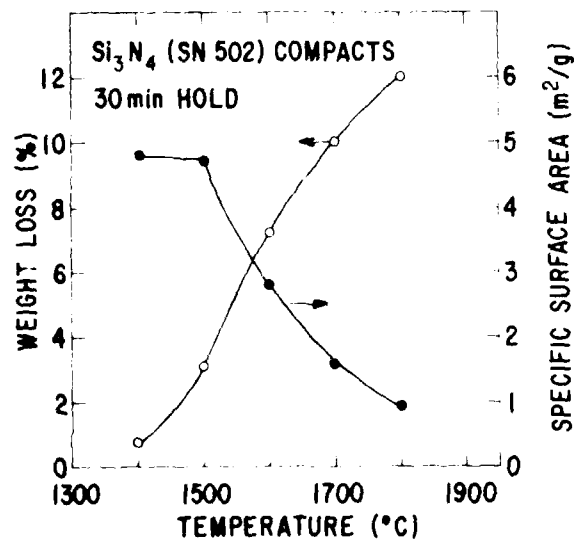
Figure 6. Weight Loss and Specific Surface Area As a Function
of Temperature for (SN-502) Si_3N_4 Compacts Fired
for 30 Min in N_2

15

The fired compacts of either starting powders did not undergo any shrinkage up to 1800°C and were weakly bonded together or crumbly. Microstructures of the fired compacts of SN-402 powder are presented in Fig. 7 and show the fine grain-fine pore structure of a specimen fired at 1300°C (Fig. 7A) as compared to the development of a large grain-large pore structure in a specimen fired at 1700°C. The "apparently" large (~2 μ), equiaxed grains observed in Fig. 7B are in fact dense regions composed of several faceted grains, as observed in Fig. 7C. The grains within a dense region appear to be well-bonded together, but there appears to be little bonding (or necking) between the dense polycrystalline regions. Another interesting result was that the fired compacts were primarily composed of α-Si_3N_4 even up to 1800°C. For example, compacts of SN-402 and SN-502 powders fired at 1800°C for 30 min in N_2 were composed of about 90% α +10% β-Si_3N_4 and 70% α +30% β-Si_3N_4, respectively, with no evidence of any free silicon or silica.

4. Discussion

The observation that large weight losses up to 18% are accompanied by no change in the external dimensions of the fired compact strongly suggests that material loss occurs throughout the bulk of the porous ($\sim65\%$ porosity) sample. The similar weight loss of Si_3N_4 compacts made from starting powder containing 3.14 and 0.7 wt% oxygen and fired at 1800°C suggests that the major portion of material loss is caused by thermal decomposition of Si_3N_4 into Si and N_2 and not by oxygen removal according to reactions (1) and (2). This suggestion is strengthened by the fact that a compact of (SN-402) Si_3N_4 powder fired at 1700°C for 30 min in nitrogen (10 ppm oxygen impurity) had a weight loss 14% but still had an oxygen content of 1.8 wt%. From this information the maximum amount of weight loss expected from reactions (1) and (2) can only be about 6 wt%, based on the initial (3.14 wt%) and final oxygen contents of the Si_3N_4. Finally, when a rapid heating rate of 300°C/min was used instead of the slow heating rate of 4°C/min, the observed weight loss was nearly the same.

The finding that large weight losses occur simultaneously with large reductions in specific surface area over the same temperature range (between 1100 and 1800°C) in a nitrogen environment suggests that the weight loss of compacts is sensitive to surface area and temperature. The sensitivity of weight loss to the available surface area is demonstrated by the experiment in

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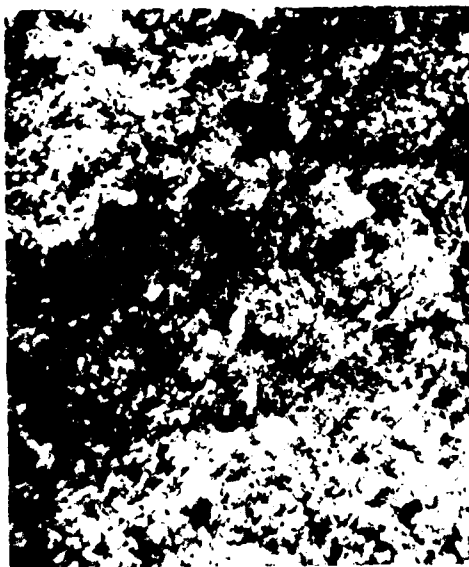
(A)
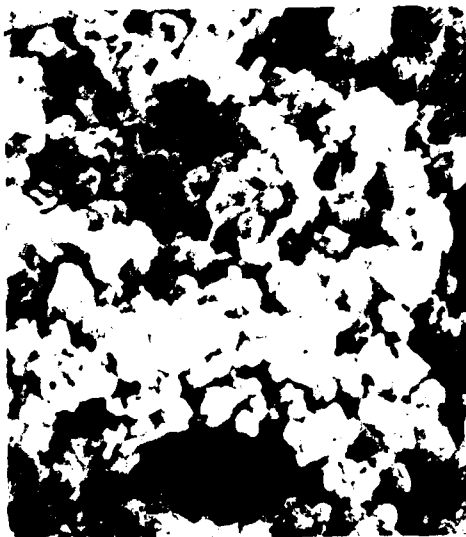
(B)

Figure 7. Scanning Electron Micrographs of Fractured Surfaces of (SN-402)
Compacts Fired 30 Min in N_2 at (A) 1300°C, 2,000X, (B) 1700°C,
2,000X, and (C) 1700°C, 10,000X

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(C)

Figure 7. (Continued)

which the resulting weight loss and specific area of an SN-402 compact fired at 1800°C for 30 min were ~15% and 0.8 m^2/g, respectively (see Fig. 5), but were only 0.7% and 0.7 m^2/g upon refiring the same specimen for another 30 min at 1800°C in the same furnace.

The large weight losses observed and the fact that a considerable amount of grain (particle) growth and pore growth takes place without any macroscopic shrinkage lead to the conclusion that the sintering of pure Si_3N_4 powders having average particle sizes between 0.15 and 0.4 μ is prevented by high vapor transport and/or thermal decomposition. This deduction is, so far, based on the use of two relatively pure Si_3N_4 powders, one amorphous and the other crystalline α-Si_3N_4, derived from the reaction between $SiCl_4$ and NH_3. If sintering is kinetically limited by a high ratio of matter transport by vapor phase transport as compared to volume and/or grain boundary transport, then a practical approach to densify pure Si_3N_4 is to start with Si_3N_4 powder having an average particle size <0.15 μ so that there will be a high probability for macroscopic shrinkage at temperatures at or below 1400°C, the temperature above which appreciable weight loss is detected (see Figs. 5 and 6). The preparation of finer (<0.15 μ) Si_3N_4 powders and the effect of additives which may permit solid state sintering of Si_3N_4 will be discussed below. If the thermal decomposition of Si_3N_4 is responsible for its nonsinterability, then both thermodynamic (surface energy) and kinetic considerations may be responsible. High nitrogen pressures (~5 MPa) would be expected to suppress the thermal decomposition of Si_3N_4 into Si and N_2 and, therefore, enhance the possibility of sintering. Some experiments on this very topic have been carried out and will be discussed in the next section.

The weak "intergranular" bonding or crumbliness of fired compacts of Si_3N_4 raises several important questions. Since it is mandatory to have good intergranular bonding for solid state sintering, it becomes important to determine if it is possible to obtain strong intergranular bonding in pure Si_3N_4. Is the poor intergranular bonding related to thermal decomposition of Si_3N_4 or to impurities such as chlorine? We hope to answer these questions once fine, high-purity Si_3N_4 is prepared and evaluated in our laboratory.

Another interesting point is that for the two powders investigated α-Si_3N_4 remained stable at temperatures up to 1800°C whereas Si_3N_4 powder[6] derived by the reaction between SiH_4 and NH_3 converted almost entirely into elongated

grains of β-Si_3N_4 at 1800°C in nitrogen. This evidence may suggest that impurities, notably chlorine, probably stabilize α-Si_3N_4 at very high temperatures, as reported by Morgan[7].

6. Effect of High Nitrogen Pressures

Several experiments were carried out on Si_3N_4 (SN-402) compacts at about 5 MPa (50 atm) to determine if the thermal decomposition of Si_3N_4 could be sufficiently suppressed to permit sintering. Temperatures above 1800°C were employed to enhance diffusional processes which may activate sintering. An oxygen partial pressure much lower than 1 Pa, which was used for the previous experiments in flowing nitrogen, was employed to minimize the possible oxidation of Si_3N_4. Experiments were conducted in a water-cooled tungsten resistance furnace having a hot zone 8 cm in length and 2.5 cm in diameter. Temperature was measured by optical pyrometry by sighting on the specimen surface. The gaseous environment was a 95% N_2 + 5% H_2 mixture having an oxygen content of about 2 ppm. This gas was pressurized and maintained at a total pressure of 5 MPa during the experiment.

In the first experiment a Si_3N_4 compact was fired for 45 min at 1850°C in 4.7 MPa of nitrogen and 300 pPa (3 x 10^{-15} atm) of oxygen. The fired compact was crumbly and exhibited a linear shrinkage of about 1%, weight loss of 10%, and specific surface area of 1.1 m^2/g. The relative bulk density of the fired compact was 33% as compared to 36% for the green compact. X-ray diffraction analysis showed that the fired compact consisted of about 70 wt% α-Si_3N_4 and 30% β-Si_3N_4.

The weight loss of 10% for the compact fired at 1850°C in 4.7 MPa of nitrogen is about the same weight loss measured for a compact fired at 1550°C in 0.1 MPa (1 atm) of nitrogen. This weight loss may be due to the thermal decomposition of Si_3N_4 into liquid silicon and nitrogen, but the subsequent loss of liquid silicon does not proceed via pure silicon vapor. If so, tungsten silicides would have been expected to form in the tungsten heating element because a low temperature eutectic also exists in the W-Si system[8] at 1392°C. This finding and the observation that a creamy white, condensate containing Si and Cl (H, N and O cannot be detected by the solid state X-ray detector on the SEM) deposited in the cold sections of the furnace suggested that silicon-bearing molecules, such as Si_xN_y, and/or Si-Cl-N-bearing molecules may exist in the system but not pure Si vapor species. On the other hand, the

weight loss of 10 wt% observed corresponds exactly with the weight loss expected
by the removal of all of the initial oxygen impurity (3.14 wt%) by reaction (2),
which is the reaction between Si_3N_4 and SiO_2 to give SiO and N_2. The extent
of this reaction, or reaction (1), will be determined by measuring the residual
oxygen content of the fired compact. Neither these reactions nor the thermal
decomposition reaction can, however, account for the Cl loss from the sample
during firing.

The microstructure of the fired compact is shown in Fig. 8. In Fig. 8A
the equiaxed solid regions have an average size of about 2 μ and are composed of
α-Si_3N_4 grains while the elongated grains, about 1 to 2 μ long and 0.2 to 0.3 μ
in diameter, are β-Si_3N_4, as determined by electron diffraction patterns. The
polycrystalline α-Si_3N_4 regions shown in Fig. 8B appear to be dense and contain
thermal grooves at the grain boundaries. This finding plus the appearance of a
certain amount of faceting on the surface of the grains indicate that geometrical
equilibrium is nearly approached because of minimization of the surface free
energy.

A second experiment using high nitrogen pressure was designed to reduce
the weight loss of Si_3N_4 by enclosing the compact inside a BN crucible with a
screw lid. Again, the total pressure of the 95% N_2 + 5% H_2 mixture was 5 MPa.
Unfortunately, because of problems associated with temperature control, the
temperature reached 1975°C for 5 min. Observation of the fired material and a
measured weight loss ∿60% indicated that complete decomposition of Si_3N_4 occurred.
There was a mixture of black and white material inside the BN crucible which was
identified as silicon and β-Si_3N_4, respectively, by X-ray diffraction. The
silicon was present in the form of spherical particles, on many of which a layer
of fine whiskers of β-Si_3N_4 grew. The β-Si_3N_4 phase is believed to have formed
from the reaction between liquid silicon and high pressure nitrogen during
cooling because the large weight loss observed (∿60%) is higher than that pre-
dicted (∿40%) for complete decomposition of Si_3N_4. The high weight loss
observed is caused by diffusion, hence loss, of gaseous silicon-bearing species
out of the BN crucible which deposit on the cold surfaces of the furnace walls.

A reaction zone was observed on the tungsten heating element in the
vicinity of the BN crucible. X-ray diffraction analysis showed the presence of
WB, WB_2 and W in the reaction zone with no indication of any tungsten silicides,
again indicating that pure silicon vapor species do not exist at high nitrogen

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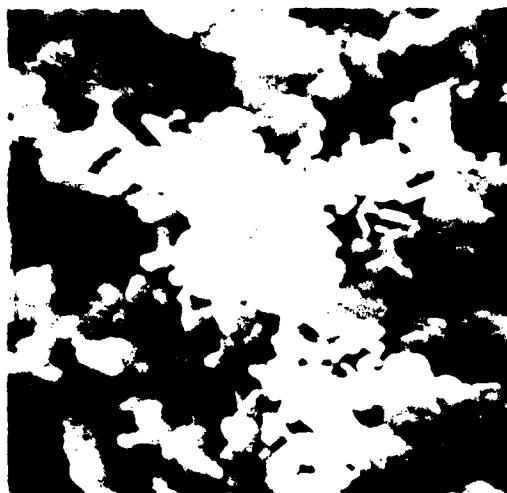
(A)
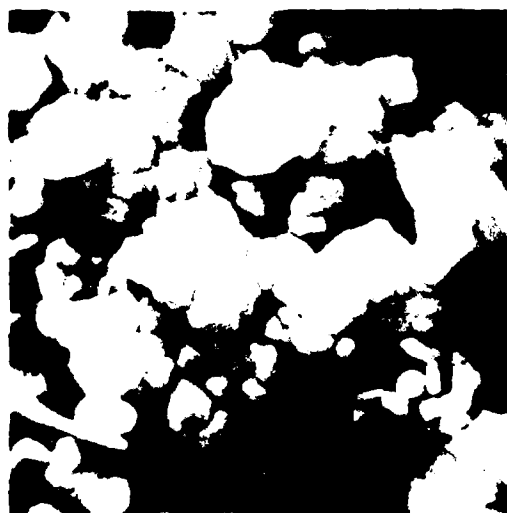
(B)

Figure 8. Scanning Electron Micrographs of Fractured Surfaces of a (SN-402)
Compact Fired at 1800°C for 45 Min in 4.7 MPa (47 atm) of N_2.
(A) 5,500X and (B) 10,000X

pressures. This reaction between BN and the tungsten heating element probably changed the electrical resistance of the heating element and was responsible for the difficulty in maintaining temperature control. As a result, BN does not appear to be a compatible crucible material for Si_3N_4 in this tungsten furnace at high temperatures.

In summary, the use of a high nitrogen pressure of 5 MPa and a low oxygen partial pressure of 100 pPa at temperature above 1800°C did not permit more than 1% linear shrinkage of pure Si_3N_4 compacts but did considerably reduce the weight loss below that found when 0.1 MPa of nitrogen is used. Under these conditions grain growth and pore growth occur in the absence of much macroscopic shrinkage, suggesting that vapor phase transport and/or thermal decomposition still dominate structural transformation during firing. Furthermore, the high nitrogen pressure of 5 MPa had little effect on improving the strength, i.e. the intergranular bonding in the fired compact.

V. HIGH PRESSURE, HOT PRESSING OF Si_3N_4 POWDERS

A. Objective

Attempts to consolidate silicon nitride without "sintering aids" under hot pressing conditions have shown, with one exception, no densification at all[7]. The products were generally friable, poorly bonded compacts, with densities around 50% of theoretical. Our results on hot pressing SN-402 and SN-502 powders of Si_3N_4 confirm these observations. The one exception was the densification of very pure Si_3N_4 derived from silicon diimide to about 90% at 1800°C and 4 MPa (6000 psi)[7].

The absence of densification in Si_3N_4 as well as in C, BN, AlN and SiC is probably related to low atomic diffusivity. There is, unfortunately, no information on nitrogen or silicon diffusion in Si_3N_4 to directly support this assumption. The one indirect piece of evidence for the very low diffusivity has been the virtual absence of creep in CVD Si_3N_4 at 1550°C and 70 MPa (10,000 psi) studied in bending[6].

The absence of bonding, i.e. interparticle contact growth, is more diffucult to account for. Si_3N_4 is known to have a relatively high vapor pressure and hence particle growth is expected, and is indeed observed on heat treatment of powder compacts. The same transport mechanism should bring about interparticle contact growth as is observed in other substances with relatively

high vapor pressure, such as AlN, NaCl, MoO_3, etc. Contrary to expectation, bonding in pure Si_3N_4 is, in most cases, negligible. Hot-pressed Si_3N_4 powders can be scratched with a fingernail and crumbled between fingertips. On the other hand, Si_3N_4 formed in situ by nitridation of silicon seems to exhibit ample intergranular bond formation. This peculiar behavior of Si_3N_4 is inconsistent with the understanding of the physical processes involved in sintering and is obviously the key problem in the study directed towards developing a consolidation process for this material.

We decided to study this problem by consolidation of selected Si_3N_4 powders under diamond forming conditions followed by heat treatment of the resulting compacts. From these experiments it was hoped to obtain qualitative information on atomic mobility in Si_3N_4 at high temperatures and, of course, on the stability of intergranular bonds formed under these extreme conditions.

Densification under diamond forming conditions would not be, however, a sufficient criterion for bonding and atomic mobility. Nadeau[9], who studied high pressure hot pressing of silicon carbide, has observed that with some powders 95% of theoretical density could be obtained at 5 GPa (50 kb) and temperatures <1500°C by rearrangement and fragmentation of grains and that the resulting compacts had a dense ceramic appearance. However, such compacts could not be satisfactorily ground and polished, showed very low microhardness values and specific microstructures. Therefore, microstructural studies, indentation hardness and X-ray diffraction analyses were selected as the prime characterization methods. In addition, we intended to investigate the compacts by annealing them at various temperatures to find out whether or not grain growth would occur. Grain growth in pure Si_3N_4, if detected, would be sufficient evidence that enough atomic mobility exists to make consolidation by sintering processes possible, at least in principle.

The work, still in progress, is reviewed below. The initial experiments where a number of technical problems were encountered, such as Si_3N_4 interaction with the cell components, specimen fragmentation on pressure relaxation, unknown powder purity, etc., were omitted.

B.   Experimental

The apparatus and procedure for ultra-high pressure consolidation of Si_3N_4 powders has been essentially the same as used for diamond synthesis and has

been adequately discussed previously[10]. The only necessary change has been the use of a boron nitride liner within the carbon heater to prevent Si_3N_4-carbon interaction. The liner consisted of a thin-walled tube and bottom and top spacers, all of which were machined from commercial BN stock to fit into the carbon heater. Pellets 0.95 cm x 0.64 cm were prepressed from the powders, repressed isostatically at 200 MPa (30,000 psi) and prefired in nitrogen or NH_3 at 1200°C. Two of these fired pellets would fit into the cell. Preliminary experiments showed that 1400°C was the lowest temperature that could be used to obtain good bonding and densities. Therefore, the present series of experiments was carried out in the region 1400-1600°C. Temperature was obtained from power readings and calibrations and was accurate within ±50°C. The specimens were held at temperatures for 20 min under 5.5 GPa.

Thus far, the high pressure, hot pressing experiments were carried out using four Si_3N_4 powders. Powder 1 was produced in our laboratory and synthesized from SiH_4 and NH_3 (see the following section). This powder was a light brown, amorphous material having a specific surface area of 26 m^2/g and oxygen content <0.5 wt%. Powder 2 was a white, amorphous material derived from ammonolysis of $SiCl_4$ and had a specific surface area of 43 m^2/g and an undetermined amount of oxygen impurity. Powder 3 was Sylvania SN-502 material described earlier in Section III-A. It is a light tan, crystalline powder (94% α-Si_3N_4 + 6% β) having a specific surface area of 4.5 m^2/g and an oxygen content of about 1%. Powder 4 is the SN-502 powder processed by vibratory milling for 6 hrs with cemented tungsten carbide balls in a plastic jar in benzene. The tungsten carbide pickup corresponded to less than 1 wt% W.

The pills obtained after compaction are about 0.6 x 0.3 cm in size and are rarely free of cracks. Usually severe cracking occurs on pressure relaxation due to differences in compressibility of the cell components. The typical appearance of a specimen crossection is shown in Fig. 9. After recovery the specimens were boiled in concentrated HCl to remove residue of adherent BN. Density was determined by liquid displacement or by floating of specimen fragments in mixtures of CCl_4 + CH_2I_2 of known density. However, neither technique is accurate in this situation because of specimen cracking, and errors of ±0.05 g/cc are anticipated. The cracks made it also impossible to determine accurately whether the specimens had open porosity or not. Phase composition was determined by X-ray diffraction on a diffractometer. For metallography, specimens were mounted, ground and polished with 3 µ diamond grit. No satisfactory

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Figure 9. Polished Section of a Typical Si_3N_4 Specimen
Compacted at 5 GPa and 1550°C   30X

etchant was found and almost every specimen responded differently to those tried. Three chemical etchants were tried on Si_3N_4 with limited and variable success: (a) a boiling solution of 5 cc HNO_3 (concentrated), 30 cc HF (50%) and 25 cc H_2O_2 (30%), (b) a boiling solution of 15 cc HF (50%), 45 cc HNO_3 (concentrated) and 45 cc acetic acid and (c) a melt of KOH-NaOH at 280°C. Etchant (c) caused severe pitting at particular spots and no effect elsewhere. Etchants (a) and (b) revealed some grain boundaries only. The character of the grooves (spotty appearance) obtained with these etchants is similar to the character of grain boundaries which contain SiO_2 in hot-pressed SiC[11], and it is possible that in the present case the reagents attacked only segregated impurities.

The difficulties with etching and the very limited amounts of experimental material made grain size measurements uncertain. Nevertheless, by combining TEM (double stage replicas), optical microscopy and SEM fractography estimates of grain size could be made and are reported in Table II.

Annealing experiments were done by packing the pills into Si_3N_4 powder in a small BN crucible and heating in a carbon resistance furnace in nitrogen at about 1650°, 1750° and 1850°C for 40 min. However, none of the specimens survived 1850°C without serious degradation.

C. Results

In the following, the response of each of the four Si_3N_4 powders and the characterization of the resulting microstructure are discussed separately. Some of the results are summarized in Table II.

Figures 10 and 11 give TEM of replicas of a fracture surface and polished and etched surface of specimen 2. This specimen contained grains of free silicon which were revealed as a result of etching (rounded white spots, Fig. 11). The silicon phase in this specimen does not tend to distribute itself along grain boundaries, but forms discrete grains. Their rounded shape suggests that the ratio of the grain boundary energy of Si_3N_4 to the Si-Si_3N_4 interfacial energy is close to 1.

Very few pores can be seen and confirms the high density value measured (3.11 g/cc). The grain size was estimated from Fig. 11 to be near 0.2 microns which is about the maximum particle size of the starting powder (see Fig. 19), implying that little grain growth occurred during the high pressure consolidation. On the other hand, interparticle bonding is excellent as shown by the

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TABLE 11

Result of hot Pressing of Si_3N_4 at 5 GPa

Spec. No.	Starting Powder	Pretreatment of the Pressings	Consolidation Temperature °C ±50	Appearance	Density g/cc	Phases Present	Micro-hardness (Knoop) @ 200g load	Grain size Estim.(μ)
1	1	NH_3, 1200°	1100	Dark gray, fragmented	2.75	n.d.	1100	-
2	1	NH_3, 1200°	1500	Dark gray	3.11	$\beta\text{-}Si_3N_4$ Si trace*	3080	<0.2
3	1	N_2, 1200°	1600	Dark gray	3.05	$\beta\text{-}Si_3N_4$ Si trace*	3000	<0.2
4	2	NH_3, 1200°	1500	White, fragmented	2.57	n.d.	n.d.	n.d.
5	2	NH_3, 1300°	1550	White, cracked	2.90	$\beta\text{-}Si_3N_4$	250	bimodal 0.2 & 0.8
6	3	N_2, 1200°	1500	Ivory, cracked	2.65	n.d.	n.d.	n.d.
7	3	N_2, 1200°	1550	Ivory, cracked	2.89	$\alpha\text{-}Si_3N_4$ <10%β	1200	<0.5
8	4	N_2, 1200°	1500	Gray, cracked	3.15	$\text{-}Si_3N_4$	2500	>1
9	4	N_2, 1200°	1550	Gray, cracked	3.19	n.d.	n.d.	n.d.

* Less than 5%

Figure 10.   TEM of a Replica of a Fractured Surface of Si_3N_4
Compacted at 5 GPa and 1500°C.   Specimen 2 in
Table II   30,000X

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Figure 11. TEM of a Replica of a Polished and Etched Surface. White Spots Correspond to Leached-Out Silica Grains. Specimen 2   30,000X

Knoop indentations (200 g). The value of 3080 found is in fact higher than those previously reported for dense Si_3N_4 [12,13]. Another interesting feature is the predominantly transgranular fracture in this specimen (Fig. 10). Silicon nitride conventionally hot pressed with additives is known to fracture intergranularly.

Specimen 3 was annealed 40 min at 1650, 1760 and 1850°C. No change in appearance and grain growth was detected by optical microscopy (2,000X) after exposure to 1760°C (Fig. 12A and B). The specimen degraded on annealing at 1850°C as a result of crack growth due to evaporation and was not evaluated metallographically.

Specimen 4 fragmented on removal from the pressing cell. This fragmentation could be partly suppressed by pretreating the precompacted pill at higher temperature, 1300°C, for 1 hour (specimen 5). However, it is likely that particle coarsening occurred in this extremely fine starting powder at this temperature. Therefore, the grain size estimated from the micrograph on Fig. 13 does not truly indicate growth during consolidation. Although about 90% of the theoretical density was achieved, bonding was poor as reflected by the low microhardness value. This suggests a case of a high degree of compaction achieved primarily by fragmentation and rearrangement under extreme pressure, similar to that observed by Nadeau on SiC. In other words, the atomic mobility was negligible in this Si_3N_4 sample at 1550°C.

The fracture surface of specimen 7 is shown in Fig. 14A and B. This specimen was well bonded and had a relatively low microhardness most likely related to the large volume fraction of round, nearly spherical pores. These round pores suggest that atomic mobility during the microstructure formation was appreciable. A crude estimate of grain size ∿0.5 μ was made from the fractographs because no information on grain size could be obtained on this specimen by polishing, etching and replication for TEM. The etching treatments revealed only segments of some grain boundaries. It is speculated that the boundary pattern revealed by etching is due to segregated silica, i.e. only silica in grain boundaries was attacked by the etchant. This may be the case since no change in the pattern was observed by extended exposure to the etchant. In addition, a few sizable (∿50 μ) inhomogeneities having a much lower reflectivity that Si_3N_4 were observed in the as-polished surface of this specimen and

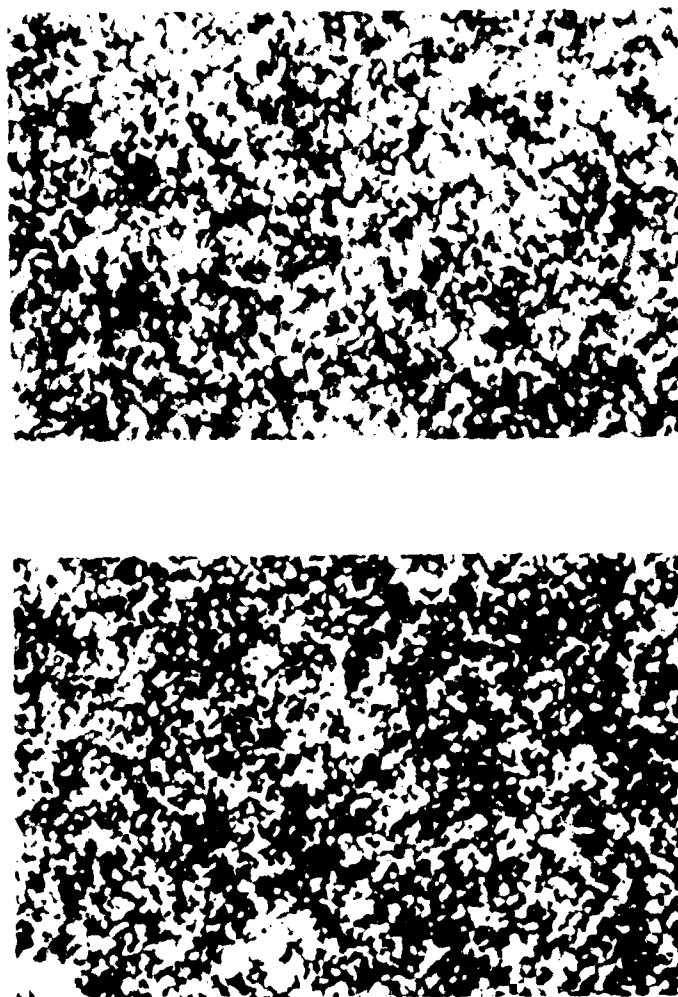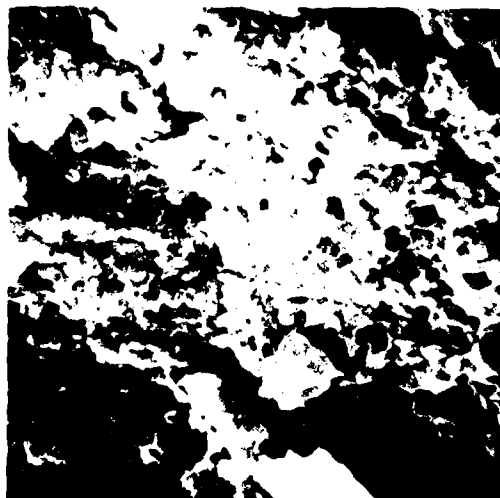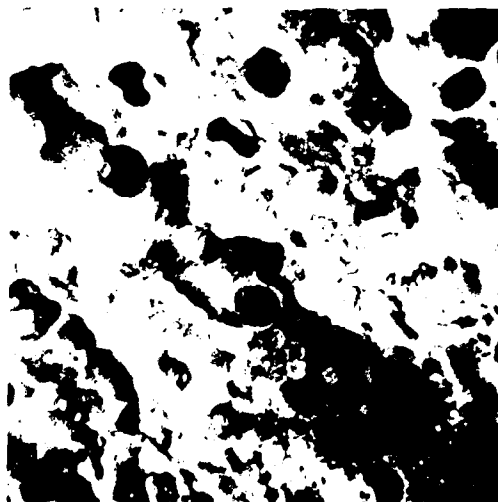Figure 12. Hot-Pressed Si_3N_4 (Specimen 3) (A) As Prepared and (B) After Annealing at 1760°C for 40 Min. Phase Contrast Micrographs of a Polished Surface 2,000X

Figure 13. Microstructure of Poorly Bonded, Hot-Pressed Si_3N_4 (Specimen 5). TEM, Double Stage Replica   30,000X

(A)

(B)

Figure 14. Si_3N_4 (SN-502) Hot Pressed at 1550°C and 5 GPa. SEM
of a Fractured Surface, (A) 5,000X and (B) 10,000X

were found to contain only silicon by the electron microprobe. This evidence strongly suggests that the particles are SiO_2.

The annealing of this specimen at 1650°C led to expansion and delamination as shown in Fig. 15. This resulted from opening of numerous cracks perpendicular to the pressing direction and not from separation of individual grains as shown in Fig. 16. This photograph also shows that very little grain growth occurred.

The processed SN-502 powder 4 gave rise to specimens (8 and 9) with the highest densities by high pressure, hot pressing. These specimens were well bonded together and exhibited a microhardness value of 2500. Very few small pores can be observed in the fracture surface of this specimen (Fig. 17).

Specimen 8 was the only one which was composed of α-Si_3N_4. All other specimens were β-Si_3N_4 only. There was considerable difficulty in obtaining a good grain boundary etch so that little information on grain size could be obtained. Nevertheless, the replicas (see Fig. 18A and B) together with results of SEM seem to indicate that substantial grain growth occurred on annealing the specimen at 1750°C. It should be pointed out that there was no expansion or "bloating" of this sample during high temperature annealing. Thus it appears that the processing of the powder with cemented carbide balls dramatically changed the microstructure and its high temperature behavior.
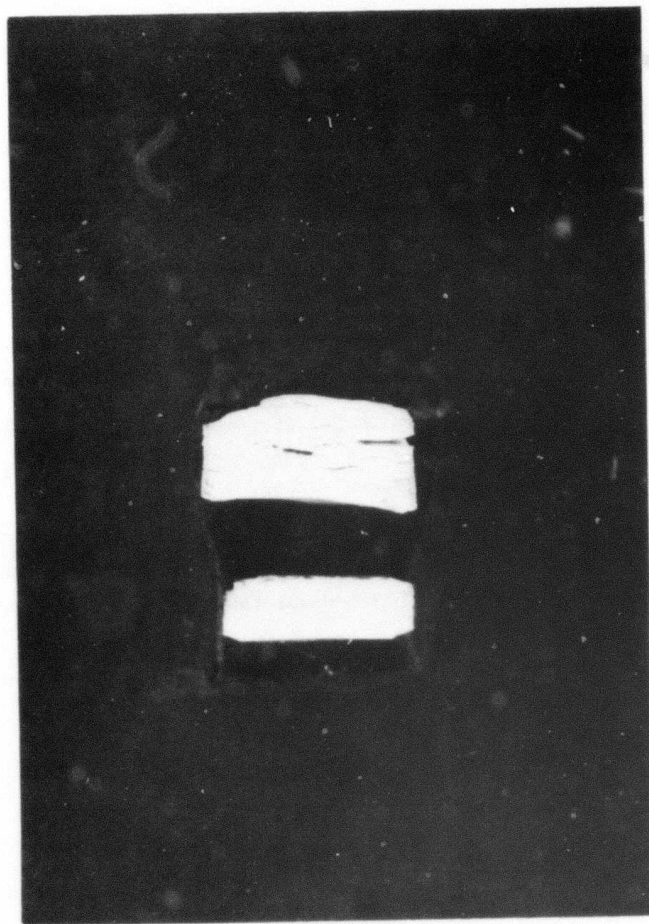
Figure 15. A Piece of Specimen 7 Before (Lower Specimen)
and After Annealing at 1650°C   6X
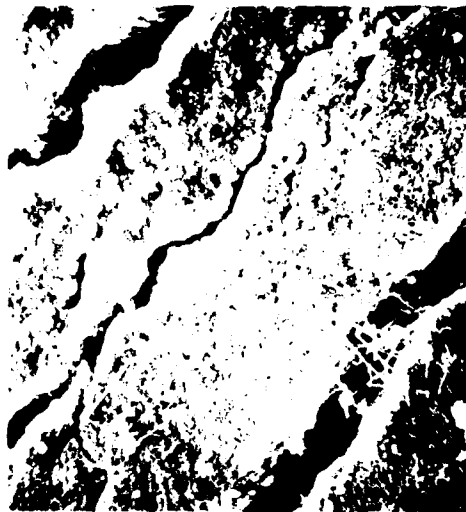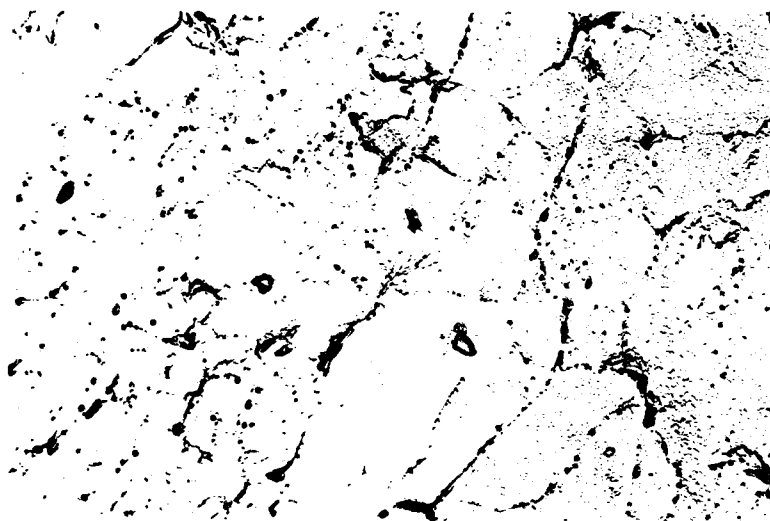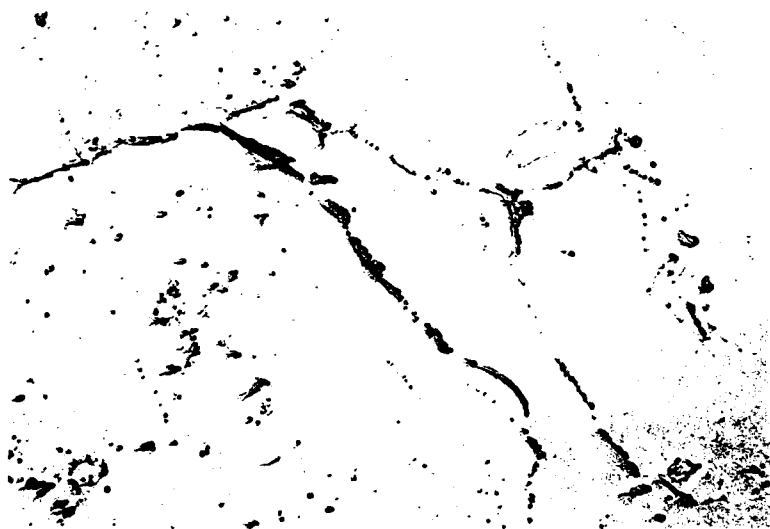
Figure 16.   SEM of Specimen 7 After Annealing at 1650°C
10, 000X

Figure 17.   SEM of a Fractured Surface of Specimen 8
Which was Hot Pressed From Processed
SN-502 Powder   5, 000X

(A)

(B)

Figure 18. Polished and Etched Surface of Specimen 8 (A) As-Pressed
and (B) Annealed at 1750°C.   TEM Double Stage Replica
24, 000X

VI. THE EFFECT OF CHEMICAL ADDITIONS ON THE FIRING BEHAVIOR OF Si_3N_4 COMPACTS

A. Introduction

The inability to densify and cause intergranular bonding in relatively pure Si_3N_4 compacts by sintering and hot-pressing methods led to the investigation of the effect of chemical additives on the firing (sintering) behavior of Si_3N_4. The additives selected so far (B, BN and C) as well as the reaction products between these and Si_3N_4 in a nitrogen atmosphere have a melting point or decomposition temperature higher than the decomposition temperature of ~1900°C for Si_3N_4. The major objective is to attempt to densify Si_3N_4 by a solid state sintering process instead of by the method of liquid phase sintering or hot pressing in the presence of a liquid phase.

The judicious selection of chemical additives for Si_3N_4 was based on the findings of the first year's work[6] concerning the sintering behavior of covalently bonded β-SiC and Si. That work demonstrated that the addition of small amounts of boron to unsinterable powders of both β-SiC and Si containing carbon and to unsinterable powders of pure Si gives rise to fired compacts characterized by a higher specific surface area and a finer grained-finer pore structure, compared to the undoped material, which enables a greater amount of densification during firing. A certain fraction of the small B atoms (atomic radius ~0.88 A) dissolve into the β-SiC and Si lattices at elevated temperatures. The net result of the effect of boron is the increase in the ratio of matter transport by volume and/or grain boundary diffusion as compared to vapor phase and/or surface transport during solid state sintering. Thus by monitoring the development of microstructure, specific surface area, weight loss and dimensional changes of doped-Si_3N_4 compacts during firing, it was hoped that effective dopants could be identified for the solid state sintering of Si_3N_4.

Before work started on the addition of chemical additives to Si_3N_4, an effort was made to reduce the weight loss during the firing of "pure" Si_3N_4 compacts by packing Si_3N_4 powder around the green compact inside a BN crucible with a screw-top lid. After firing at 1800°C for 30 min in N_2, the weight loss was only about 7%, compared to 15% when a BN crucible is not used. This large reduction in weight loss was probably due to either (1) a larger diffusion boundary layer thickness present in the closed (but not sealed) crucible, thereby

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creating a lower flux of vapor species leaving the Si_3N_4 compact and/or (2) contamination from the BN crucible. The microstructure of a Si_3N_4 compact fired in the BN crucible at 1800°C is shown in Fig. 19. A fine-grain structure is apparent from the photograph as well as from the measured specific surface area of 10.9 m^2/g. The preservation of this high specific surface area in Si_3N_4 compacts at 1800°C and the fact that boron permits high specific surface area in fired compacts of both β-SiC and Si containing carbon suggested that boron and perhaps carbon should be added to Si_3N_4.

B.   Experimental Procedure

The chemical additives tried thus far were B, BN and B + C. The specific surface areas of the boron and carbon were 40 and 300 m^2/g, respectively, whereas that of the BN was not determined. Small percentages of each additive (<5%) were added to the "as-received" (SN-402) Si_3N_4 powder and mixed with benzene in a polyethelene bottle on a mixer/mill for 30 min. The dried powder was isostatically pressed into disc-shaped compacts, 1.5 cm in dia x 0.22 cm thick, each weighing about 0.5 g. The green compacts of a given composition were fired on a SiC setter and in the same furnace described earlier for the sintering experiments.

A maximum temperature of 1800°C was adopted as part of the standard firing cycle because (1) α-Si_3N_4, which develops from the SN-402 amorphous powder, remains stable up to 1800°C, (2) the high temperature of 1800°C may enhance the mobility of the atomic species of Si_3N_4 and (3) such a high temperature may be required to increase the solubility of the chemical additive so that diffusional processes associated with sintering (shrinkage) can take place faster in a disordered solid solution.

C.   Results and Discussion

The compositions studied and the results of the characterization of the fired compacts are given in Table III. The addition of 1 wt% boron dramatically increased the specific surface area of the fired specimen from 0.8 to 13.6 m^2/g and reduced the weight loss from 15 to 11%, as compared to fired, undoped Si_3N_4. By increasing the boron content to 4 wt%, the specific surface area of the fired material was very high, 29.5 m^2/g. This value of specific surface area is higher than that of the starting compact and is difficult to account for. Since capillary condensation of nitrogen probably cannot account for such a high surface area, it may be that BN forms with a very high surface area from the nitridation of boron during firing. Although high specific surface areas were achieved with the boron additions of 1 and 4%, there still was no shrinkage.

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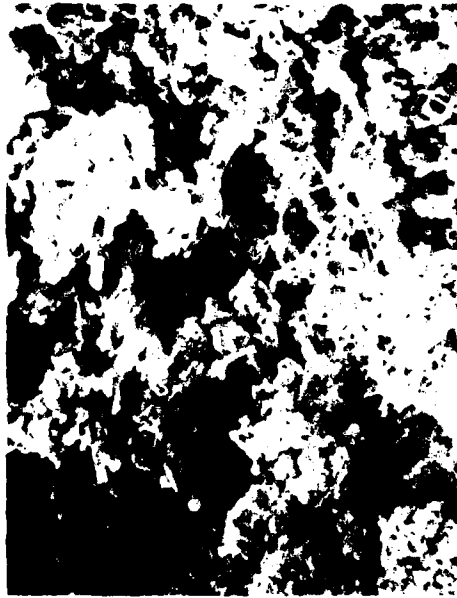
Figure 19. SEM Photomicrograph of a Fractured Surface of a Compact
of SN-402 Powder Fired in a BN Crucible at 1800°C for
30 Min in N_2 2,000X

TABLE III

The Effect of Additives on Si_3N_4 (SN-402) Compacts

Fired at 1800°C for 30 min in Nitrogen

Composition (wt%)	$\Delta W/W_0$ (%)	S.A. (m^2/g)	$\Delta L/L_0$ (%)	Phases Present
Si_3N_4	15	0.8	0	90% α + 10% B
99% Si_3N_4 + 1% B	11	13.6	0	"
96% Si_3N_4 + 4% B	8	29.5	0	"
99% Si_3N_4 + 1% BN	11	2.7	0	"
97.7% Si_3N_4 + 2.3% BN	12	3.1	0	"
96% Si_3N_4 + 3% B + 1% C	9.4	32	0.5%	"
92% Si_3N_4 + 5% B + 3% C	6.2	33	1%	"

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Furthermore, the boron dopant did permit some degree of intergranular bonding which gave the fired compacts some strength. X-ray diffraction analysis using the Debye-Scherrer technique showed that the boron at least partly dissolves in the Si_3N_4 structure because the lattice parameters of pure Si_3N_4 are $a_o = 7.7458 \pm 0.0010$ Å and $c_o = 5.6120 + 0.0007$ Å and of 1 wt% B-doped Si_3N_4 are $a_o = 7.7433 \pm 0.0010$ Å and $c_o = 5.6096 \pm 0.0008$ Å. In addition, X-ray diffraction showed no difference in the amount of β-Si_3N_4 present ($\sim$10 wt%) in the fired compacts of undoped and B-doped Si_3N_4.

The microstructure of the fired sample containing 1 wt% B is presented in Fig. 20A and B. Most of the grains are in the form of equiaxed clusters (Fig. 20B) of a variable size ranging below 1 μ. Individual grains appear to be <0.25 μ and agrees well with the corresponding grain size calculated from surface area measurements, 0.14 μ. The microstructure of Si_3N_4 doped with 4% B has not been photographed yet.

The addition of 1 and 2.3% BN to Si_3N_4 also reduced the weight loss and increased the specific surface area of the fired specimens, compared to the fired, undoped-Si_3N_4 compact. However, BN is not as effective as B in preventing grain growth (coarsening) at 1800°C.

The simultaneous addition of boron and carbon also gave rise to fired compacts with high specific surface areas ($\sim$32 m^2/g) and a small amount of linear shrinkage (<1%). Although the microstructures have not been photographed, it is again difficult to explain the high values of specific surface area observed in these fired compacts. The specific surface area of the green compact can be calculated from the starting weight fractions and specific surface areas of the Si_3N_4, B and C powders and is about 17.5 m^2/g for the composition 96% Si_3N_4 + 3% B + 1% C. This value is only $\sim$½ that measured for the compact fired at 1800°C.

The lack of extensive macroscopic shrinkage even though some boron dissolves into Si_3N_4 and permits the development of a fine-grained microstructure suggests that there is still insufficient mobility of the atomic species in Si_3N_4 at 1800°C for the compositions studied. However, several of these compositions will be hot pressed to see if densification can proceed in the solid state. Finally, these same dopants will be added to selected Si_3N_4 powders synthesized in our laboratory.

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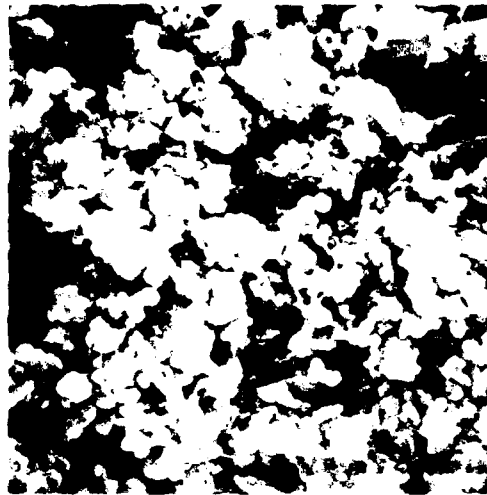
(A)
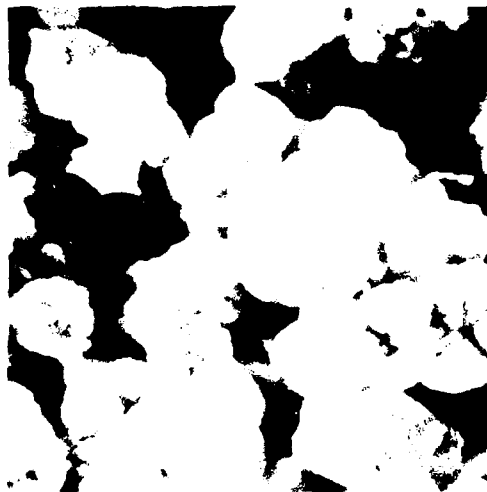
(B)

Figure 20.   SEM Photomicrograph of the Microstructure of a Compact
of SN-402 Si_3N_4 Containing 1 wt% B Fired at 1800°C for
30 Min in N_2 (A) 5, 500X and (B) 22, 000X

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VII. THE SYNTHESIS OF Si_3N_4 BY REACTION BETWEEN SILANE AND AMMONIA

A. Introduction

A reproducible starting powder of high purity, large surface area and low degree of crystallinity (amorphous) was needed for further studies on the consolidation of Si_3N_4. The only material which had been commercially available and had specifications close to those required was Sylvania's SN-402 powder. However, this powder has an oxygen content of 3.14 wt%, corresponding to about 6 wt% SiO_2, and a chlorine content <1%. Furthermore, this powder gives rise to poor intergranular bonding when sintered or hot pressed. Consequently, considerable effort was devoted towards synthesizing high purity, amorphous Si_3N_4 powders on a laboratory scale.

Two preparative routes besides nitridation of elemental silicon have been studied previously: (a) the silicon diimide route[7,14,15,16], (b) the high temperature synthesis from $SiCl_4$ and NH_3[15]. Both processes have been recently evaluated by Morgan who discussed the problems and pitfalls[7]. In short, unless ammonium chloride was completely removed from the intermediates, a chlorine-containing product resulted which did not respond to hot pressing at all, while a very pure, amorphous Si_3N_4 showed an encouraging degree of densification. In support of Morgan's conclusions, we observed that when Sylvania's SN-402 powder was heated to high temperatures a cream-colored condensate formed on the cold walls of the furnace and contained silicon and chlorine, indicating that perhaps chlorine-bearing silicon species vaporize from the powder. Morgan also suggested that the problem of chlorine could be perhaps circumvented by synthesizing Si_3N_4 from silane and ammonia. We decided to investigate this possibility.

Silane does not react with NH_3 at ambient temperatures but does react with liquid NH_3 when the reaction is catalyzed by an alkali amide[17]. The product is a condensed substance with a variable composition containing the compounds $Si(NH_2)_2NH$ and $Si(NH)_2$[18]. These compounds are very sensitive to moisture, and on contact with ambient air tend to hydrolyze. Also, the washing of of the precipitate with liquid ammonia (to remove the alkali amide) makes this reaction inconvenient as a preparative technique. We have, therefore, pursued the possibility of reacting SiH_4 with NH_3 at elevated temperatures.

B.   Experimental

The starting materials were: silane. electronic grade from Union Carbide Corp., anhydrous ammonia, dried with Ca_3N_2, and purified argon.

The gases were metered into a quartz reaction tube 3.8 cm diameter through flowmeters and separate concentric inlet tubes. The reaction tube was placed in a tube furnace and connected on the downstream end to a coaxial electrostatic separator operated between 5 and 15 kV and 0.2 to 0.5 mA. The outlet of the separator was terminated with a bubbler filled with an organic solvent which ensured positive pressure in the system. A liquid manometer indicated gas pressure in the tube.

The use of the electrostatic separator was essential because the reaction products formed a stable aerosol (smoke) from which the solid cannot be conveniently separated by other means. In the experiments, the furnace was heated to the selected temperature, the system purged with argon and the reactants were metered in. After termination of a run the system was cooled to room temperature under flowing argon and disassembled. The reaction product washed out of the tube and the separator by acetone. After drying, the collected powder was characterized by X-ray diffraction, surface area measurements, electron diffraction and microscopy and IR absorption spectroscopy. The reaction conditions of five experiments are listed in Table IV, and the results are discussed below.

C.   Results and Discussion

All the powders prepared were amorphous to X-rays; powders 1 and 2 were also amorphous to electron diffraction. A TEM photomicrograph (Fig. 21) showed that spherical particles ranged in size between 0.03 to 0.2 microns and tended to aggregate into chains and loose clusters.

I.R. spectroscopy showed one broad absorption band between 9 and 12 microns and one smaller peak at 21 microns. The absence of fine structure superimposed over these peaks is indicative of the absence of crystalline forms of Si_3N_4[16]. There are also detectable peaks at wavelengths characteristic for O-H and C-H bonding in CH_3, which probably resulted from occluded water and acetone. All the powders are readily soluble in 5% hydrofluoric acid but are insoluble in both cold and hot solutions of 15% KOH.

TABLE IV

Reaction Conditions and Characterization
of Si_3N_4 Powders Synthesized from Silane and Ammonia

| Run No.	Reaction Temp. °C	Flow rates cm³/sec			Yield g	Product color	Surface area m²/g
		Ar	NH_3	SiH_4			
1	820	4	12	3.2	18	light brown	26
2	780	4	12	3.2	14	brown	14
3	720	4	12	2	10	brown	15.5
4	920	4	12	1.2	15	light orange-brown	11.8
5	530	8	8	0.56	3	white	80

Figure 21. TEM Photomicrograph of Amorphous Particles of Powder 1
40, 000X

It was assumed that the discoloration of powders 1 through 4 resulted from the presence of amorphous silicon. By annealing these powders in nitrogen above 1400°C, the powders turned cream-white and gained weight (5 and 8%, respectively, for specimens 1 and 2). The annealing of powder 3, which had the darkest color, brought about strong X-ray peaks characteristic of silicon. The observation that annealing up to 1300°C does not bring about nitridation and that the powder is insoluble in hot 15% KOH (which readily dissolves Si) suggests that the silicon particles are coated with an impermeable layer of Si_3N_4 and are not accessible to the reagents.

Run 5 was carried out at 530°C and yielded a snow-white product. This powder had a surface area of 80 m^2/g and had many other characteristics (X-ray, I.R.) similar to the other powders. Presumably this powder is free of elemental silicon, but more characterization is necessary.

The high negative free energy of the reaction

$$3SiH_4 + 4NH_3 = Si_3N_4 + 12H_2 \tag{1}$$
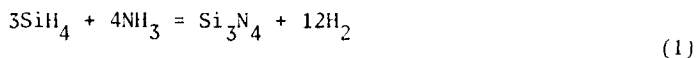
$$\Delta G_{800°K} = -6.68 \text{ MJ/kg } (-223.98 \text{ kcal/mol})$$

and the absence of any reaction below 500°C suggests that its activation energy is very high. The reaction is probably very complex and involves a number of short-lived intermediates. Above 500°C silane already begins to decompose:

$$SiH_4 = Si + 2H_2 \tag{2}$$

$$\Delta G_{800°K} = -3.58 \text{ MJ/kg } (-24.09 \text{ kcal/mole})$$

This reaction has probably an even higher activation energy so that the rate of decomposition of silane rapidly increases with increasing temperature and competes with reaction (1). The formation of Si has been observed at all temperatures above 600°C. The threshold temperature where Si is first observed depends, however, on the reactants' flow rates. The formed silicon particles undergo nitridation which is likely to occur only at the particle surfaces:

$$3Si + 4NH_3 = Si_3N_4 + 6H_2 \tag{3}$$

so that the amount of Si_3N_4 formed by reaction (3) will be controlled by the surface area of the silicon particles. The experiments indicate that once silicon has formed it cannot be fully converted into Si_3N_4 in the course of the

reaction with ammonia. In other words, at higher temperatures, above 600°C, Si_3N_4 is formed simultaneously by reactions (1) and (3), but a silicon-free product cannot be obtained. Nevertheless, it appears from preliminary evaluation of run 5 that a narrow temperature window exists between about 530°C to 570°C where reaction (1) can be carried out without or perhaps almost without free silicon formation. More detailed study of the reaction and of the product is, of course, necessary before it can be determined whether or not this process can be developed into a preparative technique.

VIII. CONCLUSIONS

Fired compacts of "pure" Si_3N_4 powders, having average particle sizes between 0.15 and 0.4 μ, undergo large (∿15%) weight losses and considerable grain growth in the absence of macroscopic shrinkage. The nearly similar weight loss of Si_3N_4 compacts made from the same starting powder but which contained different oxygen contents, 3.14 and 0.7 wt%, suggests that the major portion of material loss is caused by thermal decomposition of Si_3N_4 and not by an oxygen-removal reaction. This information leads to the conclusion that the sintering of "pure" Si_3N_4 is prevented by high vapor transport and/or thermal decomposition.

The use of high nitrogen pressures ∿5 MPa (50 atm) and low oxygen partial pressures ∿100 pPa (10^{-15} atm) at temperatures above 1800°C does not permit more than 1% linear shrinkage in "pure" Si_3N_4 compacts but considerably reduces the weight loss (thermal decomposition) below that found when 0.1 MPa (1 atm) of nitrogen is used. Since grain growth and pore growth occur without much shrinkage, it is concluded that vapor phase transport and/or thermal decomposition still dominate structural transformation during firing.

A puzzling result in sintering is the formation of weak intergranular bonds in compacts of pure Si_3N_4 fired at high temperatures in nitrogen pressures between 0.1 and 50 MPa. In addition, the conventional hot pressing of the same Si_3N_4 powders gives rise to crumbly specimens. The poor intergranular bonding may be related to thermal decomposition effects or to impurities such as chlorine. It will be necessary to determine the precise origin of this weak bonding.

Results of the hot pressing of various Si_3N_4 powders (particle size ≥0.1 μ) at high pressures (5 GPa) show that a temperature of about 1550°C is necessary for

the attainment of densification. If it is assumed that this densification occurred by a diffusion process, then it is expected that temperatures higher than 1550°C will be required to sinter pure Si_3N_4. Some of the high pressure experiments which yielded dense compacts with high Knoop hardness are encouraging. These results indicate that specific pressing conditions can yield intergranular bonding and the identification of all the factors leading to such bonding may allow densification at lower and practical pressures.

The addition of small amounts (≤ 5 wt%) of boron and both boron and carbon to Si_3N_4 permits the development of a high surface area (10-33 m^2/g), fine-grained microstructure but produces essentially no macroscopic shrinkage at 1800°C in nitrogen. For the compositions studied thus far, there is still insufficient diffusion of Si and N in Si_3N_4 to allow densification by solid state sintering.

The need for Si_3N_4 powder with higher specific surface area and purity than that commercially available led to the synthesis, on a laboratory scale, of amorphous Si_3N_4 powders with specific surface areas as high as 80 m^2/g by the reaction between silane and ammonia. At temperatures above 600°C, it is difficult to prepare Si_3N_4 powders free of silicon. Powders containing free silicon cannot be completely nitrided at temperatures below 1400°C in nitrogen. However, preliminary results indicate that Si_3N_4 powder free of elemental silicon and low in oxygen can be synthesized by the reaction between silane and ammonia in a temperature interval between about 530 and 570°C.

IX. FUTURE WORK

Efforts shall be continued in attempting to consolidate pure or doped Si_3N_4 by a solid state sintering process. For the doping studies, small amounts of chemical additives having atomic species with small covalent radii will be first tried, such as B, BN, C, Be_3N_2, AlN, Mg_3N_2, etc. Such dopants will be introduced into Si_3N_4 powders prepared in our laboratory as well as into the amorphous Si_3N_4 (SN-402) powder made by Sylvania. Sintering experiments will continue to be carried out in 0.1 MPa of nitrogen, and for promising compositions, in high pressure nitrogen (5 MPa).

Investigations on the preparation of amorphous Si_3N_4 powders with high surface area and high purity (low oxygen content) by the reaction between silane and ammonia will be continued. Furthermore, it will be confirmed that Si_3N_4

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can be synthesized without the presence of free silicon, and failing such confirmation, the nitridation conditions necessary to completely nitride the residual silicon with a minimum reduction in the surface area of the starting powder will be determined.

Additionally, efforts will continue to identify and evaluate grain growth and transport mechanisms that may account for the sintering of Si_3N_4 by (1) hot pressing pure or doped Si_3N_4 powders and following the grain growth behavior by subsequent annealing studies from which valuable information can be obtained about the expected sintering temperature, and (2) utilizing the results of a separate, but parallel, investigation on the sintering behavior and micro-structural development in NaCl since, in this material, vapor phase transport is known to compete with shrinkage mechanism(s), similar to that expected for Si_3N_4.

Finally, hot pressing experimentation with selected solute or precipitate dopings at conventional pressures will be continued and detailed work on the presintering of silicon metal and subsequent nitridation will be initiated.

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